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# Seasonal dissolved inorganic nitrogen and phosphorus budgets for two sub-tropical estuaries in south Florida, USA

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# Abstract

Interactions among watershed nutrient loading, circulation, and biogeochemical cycling determine the capacity of estuaries to accommodate introduced nutrients. Baseline quantification of loading, flushing time, export, and internal processes is essential to
 <sup>5</sup> understand responses of sub-tropical estuaries to variable climate and nutrient loading. The goal of this study was to develop seasonal dissolved inorganic nitrogen (DIN) and phosphorus (DIP) budgets for the two estuaries in south Florida, the Caloosa-hatchee River Estuary (CRE) and the St. Lucie Estuary (SLE), from 2002–2008 spanning various climatic conditions. The Land Ocean Interactions in the Coastal Zone (LOICZ) Biogeochemical Model was used to generate water, salt, and (DIN and DIP) budgets. The predicted increase in internal DIN production for the CRE vs. the SLE was associated with increased external DIN loading. Water column DIN concentrations decreased and stabilized in both estuaries as flushing time increased to > 10 d. The CRE demonstrated heterotrophy or balanced metabolism across all seasonal bud-

- gets. Although the SLE was also sensitive to DIN loading, system autotrophy and net ecosystem metabolism increased with DIP loading to this estuary. This included a huge DIP consumption and bloom of a cyanobacterium (*Microcystis aeruginosa*) following hurricane-induced discharge in 2005. Additionally, while denitrification offered a loss pathway for inorganic nitrogen in the CRE, this potential was not evident for the smaller
- and more anthropogenically altered St. Lucie Estuary. Disparities between total and inorganic loading ratios suggested that management actions should examine the role of dissolved organic nitrogen (DON) in attempts to reduce both nitrogen and phosphorus inputs to the SLE. Establishment of quantitative loading limits for anthropogenically impacted estuaries requires an understanding of the inter-seasonal and inter-annual
- <sup>25</sup> relationships for both N and P, circulation and flushing, variability in plankton community composition, and the dynamics of DON.



# 1 Introduction

Estuaries modulate the inputs of water and materials from the watershed to the coastal ocean through intense internal biogeochemical cycling. Water column concentrations of carbon (C), nitrogen (N), and phosphorus (P) vary with interactions among exter-

- <sup>5</sup> nal inputs and exports, residence time, sediment-water exchanges, and biological processes. Eutrophication disturbs these integrated processes as allochthonous and autocthonous organic carbon inputs increase in excess of balanced consumption (Nixon, 1995). This imbalance is often stimulated by loading of dissolved inorganic nutrients from the watershed (Cloern, 2001). While this model of coastal fertilization is gener-
- ally applicable, estuaries have differential capacities to accommodate introduced nutrients through a variety of factors including latitude, geomorphology, and flushing time (Dettmann, 2001; Smith et al., 2003). In particular, sub-tropical estuaries such as those in south Florida have experienced widespread coastal development accompanied by the manipulation of freshwater inflows to meet municipal, agricultural, and environmen-
- tal demands. Discharge to these estuaries introduces pulses of dissolved material that vary on synoptic to inter-annual time scales depending upon weather, climate, and watershed management (Childers et al., 2006; Dennison, 2008; SFWMD, 2012a,b).

Baseline quantification of material inputs, flushing time, downstream export, and the potential for internal production or consumption of C, N, and P is essential to better

- <sup>20</sup> understand estuarine system metabolism (Gordon et al., 1996; Giordani et al., 2008; et al., 2012). This is particularly true for coastal water bodies with heavily managed freshwater inflow subject to both short- and long-term fluctuations in discharge (Brock, 2001). In fact, sensitivity to both reduced inflows (loss of freshwater and estuarine habitats) and inorganic nutrient loading (symptoms of eutrophication) offers an appar-
- ent contradiction for estuarine management (Flemer and Champ, 2006). The amount of water and dissolved materials required to maintain optimal system metabolism with regard to CNP production and consumption should be quantified and factored into management plans for coastal watersheds.



In 1993 the International Geosphere-Biosphere Program (IGBP) and the International Human Dimensions Program on Global Environmental Change (IHDP; http: //www.loicz.org/; http://nest.su.se/mnode/) initiated a project to investigate biogeochemistry of the coastal zone (Gordon et al., 1996; Swaney et al., 2011). The Land <sup>5</sup> Ocean Interactions in the Coastal Zone (LOICZ) included a spreadsheet modeling tool designed to quantify internal C, N, and P sources and sinks in estuaries (LOICZ Biogeochemical Model or LBM; Giordani et al., 2008). LOICZ has also been a useful tool in socio-economic-political assessments of human dimensions in the coastal zone (Talaue-McManus et al., 2003; Swaney et al., 2011). The LBM has been used to investigate CNP cycling in hundreds of coastal environments (Wosten et al., 2003; Smith and Hollibaugh, 2006; Giordani et al., 2008; Yamamoto et al., 2008; Liu et al., 2009). The LBM is highly customizable depending upon the quality and quantity of data and

can be applied to any estuary without the need for detailed rate process information. In order to explore internal biogeochemical mechanisms, the overall goal of this study

- <sup>15</sup> was to generate wet and dry season dissolved inorganic nitrogen (DIN) and phosphorus (DIP) budgets for both the Caloosahatchee River and St. Lucie Estuaries (CRE and SLE, respectively) from 2002–2008. This time period was derived based on data availability and consideration for a wide range of climatic conditions. The specific objectives were to estimate DIN and DIP loading via atmospheric, groundwater, and surface
- inputs; to quantify seasonal changes in estuarine salinity and flushing time; to assess seasonal patterns of estuarine DIN and DIP concentrations; and to explore, compare, and contrast relationships between loading, flushing, concentrations, and ecosystem scale biogeochemical responses to nutrient loading within and between the CRE and SLE.



## 2 Methods

## 2.1 Study sites

Located in southeast Florida, the St. Lucie Estuary (SLE) comprises a major tributary to the ecologically and commercially valuable Indian River Lagoon (Sime 2005; Ji et al., 2007; Fig. 1). Historically, the SLE was a freshwater system exposed to the coastal ocean only through ephemeral inlets. The St. Lucie Inlet was permanently opened in 1892 to provide a connection between the SLE and coastal ocean resulting in a partially mixed estuary with a semi-diurnal tidal amplitude of ~ 0.4 m.

The past several decades have seen the SLE watershed highly altered from natural sloughs and wetlands into a system of 12 modified sub-basins through agriculture and urbanization. The SLE drains a relatively large area resulting in the large ratio between watershed and estuary surface area of 150:1 (i.e. Tampa Bay = 5.5:1). Watershed modification and periodic high-volume water releases from Lake Okeechobee have altered historical wet season and dry season discharges and patterns of nutrient loading.

<sup>15</sup> These changes in flow, salinity, and water quality are associated with increased prevalence of phytoplankton blooms, accumulation of muck-like sediments, and the loss of seagrass and oyster habitats (Sime 2005; SFWMD 2012a).

On the opposite side of Lake Okeechobee on the southwest coast of Florida is the Caloosahatchee River Estuary (CRE; Fig. 1). The CRE has been altered by human activities starting in the 1880'-s when the river was straightened and deepened (Antonini et al., 2002). The first water control structures at Lake Okeechobee (S-77) and Ortona (S-78) were completed in the 1930'-s with the last installed in 1966 at Olga (S-79; Fig. 1; Antonini et al., 2002). The meso- and poly-haline estuary downstream of S-79 also has experienced anthropogenic impacts (Chamberlain and Doering, 1998). Early descriptions of the CRE characterize it as barely navigable due to extensive shoals and

oyster bars near Shell Point (Sackett, 1888). A navigation channel was dredged with a causeway built across the mouth of San Carlos Bay in the 1960's. Historic oyster bars upstream of Shell Point were mined and removed for road construction. The present



CRE watershed (C-43 basin) is a series of linked regional sub-watersheds (SFWMD et al., 2012b). The Franklin Lock at S-79 represents the head of the CRE that extends 42 km downstream to Shell Point (SP) where it empties into San Carlos Bay and then onto the Gulf of Mexico.

## 5 2.2 LOICZ biogeochemical model (LBM)

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The LBM generates water, salt, DIN, and DIP budgets (Gordon et al., 1996; Fig. 2; Table 1). It was designed to isolate internal (non-conservative) production or consumption of dissolved CNP from the external (conservative) inputs and outputs for a spatially homogeneous estuary or estuarine segment. Data on the quantity of hydrological inputs via the atmosphere, groundwater, and surface inflow; salinity; and DIN and DIP concentrations in the upstream, tributaries and ground water, main water body, and downstream oceanic boundary from 2002–2008 were assembled for each estuary (Table 2).

The method assumes a steady state condition that balances the sum of physical in-<sup>15</sup> puts against the sum of physical outputs (Table 1; Wosten et al., 2003; Swaney et al., 2011). Volume (*V*) is introduced through rain ( $V_{rain}$ ), direct surface water discharge at the estuarine head ( $V_Q$ ), and other freshwater sources ( $V_{OFW}$ ) that were assumed to represent the sum of lateral inputs through tributaries and ground water. Physical loss terms or outputs included residual ( $V_R$ ) and exchange ( $V_X$ ) flows at the oceanic bound-<sup>20</sup> ary (Fig. 2; Table 1; Eq. 1; Gordon et al., 1996; Liu et al., 2009). While not the case for every water body, these flows were out of the CRE and SLE in all seasons (negative = out). Salt is conservative (X) and used to define  $V_X$  and flushing time ( $T_f$ ) based

upon salinity differences between the estuarine basin and the ocean boundary condition (Table 1; Eqs. 2–5). Results of water and salt budgeting are used to predict internal production or consumption of a dissolved, non-conservative substance "Y" (Fig. 2;  $\Delta$ Y in Table 1). This study examined the seasonal processing of dissolved inorganic nitrogen ( $\Delta$  DIN; gNm<sup>-2</sup>d<sup>-1</sup>) and phosphorus ( $\Delta$  DIP; gP m<sup>-2</sup>d<sup>-1</sup>). The difference between the sum of inputs and the sum of outputs is equal to internal production or



consumption under the assumption that the system is in steady-state at the seasonal time scale (Table 1; Eq. 6).

Each component of the water budget has corresponding DIN and DIP concentrations in rain (DIN<sub>rain</sub> and DIP<sub>rain</sub>), surface discharge (DIN<sub>Q</sub> and DIP<sub>Q</sub>), other freshwater sources (DIN<sub>OFW</sub> and DIN<sub>OFW</sub>), the estuary (DIN<sub>e</sub> and DIP<sub>e</sub>), and the oceanic boundary (DIN<sub>o</sub> and DIP<sub>o</sub>). The magnitude of water exchange ( $10^6 \text{ m}^3 \text{ d}^{-1}$ ) is multiplied by the corresponding concentration (mg L<sup>-1</sup>) to derive DIN and DIP loadings ( $10^6 \text{ g} \text{ d}^{-1}$ ) for all components (Fig. 2). These components are then summed and used to calculate  $\Delta$  DIN and  $\Delta$  DIP (Table 1; Eq. 7). Negative and positive values indicate net internal consumption or production, respectively, by the estuarine system.

The LBM relies upon the molar stoichiometry of the photosynthesis-respiration equation to link C, N, and P cycles in the coastal zone (Gordon et al., 1996; Smith et al., 2003; Swaney et al., 2011). Photosynthesis by algae requires 16 moles of N and 1 mole of P for 106 moles of C fixed (Table 1; Eq. 8). Since DIP does not have an air-sea exchange term it is assumed to be in stoichiometric balance with dissolved inorganic carbon (DIC) mass in the estuarine volume. Hence  $\Delta$  DIP can be converted to net ecosystem metabolism (NEM; g C m<sup>-2</sup> d<sup>-1</sup>) with NEM defined as a positive number (autotrophic) when the system consumes DIP internally (Eq. 9; Gordon et al., 1996; Yamamoto et al., 2008).

<sup>20</sup> In contrast, DIN does have an air-sea exchange component that confounds direct inter-conversion through stoichiometry. This is not particularly problematic as the LBM calculates the expected  $\Delta$  DIN ( $\Delta$  DIN<sub>exp</sub>) using  $\Delta$  DIP and the N : P ratio of particulate matter (N : P<sub>part</sub> = 16; Eq. 10). Actual  $\Delta$  DIN is calculated using the LBM DIN budgeting process and compared to  $\Delta$  DIN<sub>exp</sub>. The difference between the two values represents the relative difference between nitrogen fixation and denitrification (N<sub>fix</sub>D < 0.0 = net

denitrification; Eq. 11; Yamamoto et al., 2008; Swaney et al., 2011).



## 2.3 Application of the LBM to the CRE and SLE

Each estuarine water body was bounded and assumed to represent a homogenous volume to assess system-level internal cycling of CNP. While splitting each estuary spatially into multiple boxes and vertically into multiple layers may be both desirable

and possible using the LBM, treating each estuary as a single box was optimal for initial assessments of external loadings and internal processes. Watershed and estuary details can be found in the river-watershed protection plans for the two estuaries (SFWMD 2012a, b).

The CRE was assumed to extend from the Franklin Lock (e.g. S-79) to Shell Point approximately 40 km downstream. Estuarine surface area for the CRE is 56.9 km<sup>2</sup> with an average depth of 2.4 m (Buzzelli et al., 2013). Water control structures S-49, S-48, and S-80 provided 3 of the upstream boundaries for the SLE. The fourth upstream bound was the St. Lucie Blvd. Bridge in the North Fork which was assumed to possess flow indicative of a gated structure located farther upstream (Gordy Rd.). The downto stream boundary was at the St. Lucie Inlet. Estuarine surface area for the SLE was

22.0 km<sup>2</sup> with an average depth of 2.7 m (Buzzelli et al., 2013).

Input data for seasonal DIN and DIP budgets for the two estuaries came from a variety of sources (Table 2). Average monthly rainfall directly to the water surfaces of the CRE and SLE was queried from NEXRAD data available through the

- South Florida Water Management District (SFWMD) hydrologic data-base (DBHydro; http://www.sfwmd.gov/dbhydroplsql/show\_dbkey\_info.main\_menu). Daily freshwater inflow to the CRE measured at S-79 was averaged over each dry and wet season. Total freshwater discharge to the SLE was calculated by summing daily inflow measurements at structures S-48, S-49, S-80, and Gordy Rd. Other freshwater inflow representations of each billion of the second each discrete discharge daily and we season.
- <sup>25</sup> sentative of combined tributary and ground water input to the CRE was derived using a tidal basin watershed model developed in the Coastal Ecosystems Section at the SFWMD. By contrast, the sum of flow (F; m<sup>3</sup> d<sup>-1</sup>) from four gauged input canals (C-44, C-23, C-24, and North Fork) is approximately 70% of the total freshwater input to the



SLE (Ji et al., 2007). Thus, other freshwater input to the SLE was added as 30 % of the total summed daily discharge. Salinity (S) in the CRE was based on an average of seven mid-channel stations. Similarly, average seasonal S in the SLE was calculated using monitoring data from seven stations. While the downstream salinity value for

the SLE was taken from values observed at the farthest station (SE-11), downstream salinity used for development of CRE budgets was derived using output from a 3-D hydrodynamic model at Shell Point.

Concentrations of DIP and DIN in rain (DIP<sub>rain</sub> and DIN<sub>rain</sub>) were derived from long-term seasonal data in DBHydro and seasonal average  $NO_2^- + NO_3^- + NH_4^+$  observed in

- St. Petersburg, FL as part of the National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu/data/ntndata.aspx) from 2002–2008. Atmospheric concentrations were assumed to be regional so the same time series of DIP<sub>rain</sub> and DIN<sub>rain</sub> were applied to both the CRE and SLE. A water quality data base available from Lee County, FL provided concentrations of DIP and DIN to calculate DIP<sub>OFW</sub> and DIN<sub>OFW</sub> for
- the CRE (Table 3; http://www.lee-county.com/gov/dept/naturalresources/WaterQuality/ Pages/default.aspx). These values were also assumed to be representative of DIP<sub>Q</sub> and DIN<sub>Q</sub>. Data from seven mid-channel estuarine water quality monitoring stations (CES02-CES09) were used to calculate seasonal salinity (S<sub>e</sub>) and DIP and DIN concentrations (DIP<sub>e</sub> and DIN<sub>e</sub>) for the CRE. Nutrient concentrations in San Carlos Bay
   observed at Lee County station PI-01 provided the downstream boundary values (DIP<sub>o</sub>
- and DIN<sub>o</sub>).

Concentrations of DIP and DIN observed at S-49, S-48, and S-80 were averaged for  $DIP_Q$  and  $DIN_Q$  in the SLE (Table 4). Similar to the CRE,  $DIP_Q$  and  $DIN_Q$  were assumed to equal  $DIP_{OFW}$  and  $DIN_{OFW}$ . Data from seven mid-channel estuarine water

quality monitoring stations (SE06, HR1, SE04, SE08, SE03, SE02, SE01) were used to calculate average seasonal salinity (S<sub>e</sub>) and DIP and DIN concentrations (DIP<sub>e</sub> and DIN<sub>e</sub>) for the SLE. Nutrient concentrations observed at SE11 provided the downstream boundary values (DIP<sub>o</sub> and DIN<sub>o</sub>).



The LBM consists of MS Excel spreadsheets and macros to generate water, salt, and DIN and DIP budgets for two different time periods (e.g. dry vs. wet seasons). Annual spreadsheets were created for each of the 7 yr (2002–2008) for both the CRE and SLE (14 total spreadsheets). Each annual spreadsheet had input and result pages for both seasons with each result page including both DIN and DIP budget values. Data assembly and entry for budget calculations was the most time intensive and important part of budget development (Tables 3 and 4). Results from the LBM were collated within each estuary with overall results for the CRE and SLE combined for graphical and tabular presentation.

#### 10 3 Results

# 3.1 Caloosahatchee River Estuary

Rainfall directly to the surface of the CRE ranged between  $0.1-0.15 \times 10^{6} \text{ m}^{3} \text{ d}^{-1}$  and  $0.35-0.45 \times 10^{6} \text{ m}^{3} \text{ d}^{-1}$  in the dry and wet seasons, respectively (Fig. 3a). Total seasonal rainfall exhibited subtle inter-annual variations within both the dry and wet cate-<sup>15</sup> gories from 2002–08. By contrast, freshwater discharge to the CRE revealed long-term variability with maximum values of  $15-20 \times 10^{6} \text{ m}^{3} \text{ d}^{-1}$  in the wet seasons of 2003–2005 followed by minimal inflow for both seasons beginning in 2006 (Fig. 3b). Freshwater input from the tidal basin downstream of S-79 generally reflected patterns of surface flow except for the extreme peak in the wet season of 2005 (~ 9 × 10^{6} \text{ m}^{3} \text{ d}^{-1}; Fig. 3c).

Salinity in the CRE was inverse to freshwater discharge ranging from 7–13 in both wet and dry seasons from 2002–2004 before values ≤ 2.0 in wet season 2005 and dry season 2006 (Fig. 4a). The salinity of the CRE decreased from 20 to < 5 as freshwater inflow increased from 0.0 to 20×10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup> over all seasonal water budgets from 2002–08 (Fig. 5a). Average salinity increased to ≥ 20.0 in the dry seasons of 2007 and 2008
 when discharge was lowest and the flushing time of the CRE (*T*<sub>f</sub>) approached 50 and 70 days, respectively (Fig. 6a). Estuary-wide, average DIN concentrations exhibited



inter-annual climatic fluctuations similar to patterns of inflow from 2002–08 (Fig. 4b). DIN ranged from 0.1–0.25 mg L<sup>-1</sup> from 2002–05 before reaching 0.35 mg L<sup>-1</sup> in 2005. Average DIN concentrations decreased in both dry and wet seasons from 2006– 2008. Over all seasonal budgets, the concentration of DIN in the CRE ranged from  $0-0.35 \text{ mg L}^{-1}$  and exhibited a modest increase with external loading of DIN up to 0.06 g N m<sup>-2</sup> d<sup>-1</sup> (Fig. 5b). The relationship between flushing time and DIN concentrations were unclear although DIN was minimal (~ 0.1 mg L<sup>-1</sup>) when  $T_f = 50 d$  (Fig. 6b). In contrast to DIN, DIP concentrations in the CRE were remarkably consistent ranging from 0.03–0.12 across all seasons and years (Fig. 4c). In fact, there was no obvious relationship between either the external loading of DIP (0.0–0.025 g P m<sup>-2</sup> d<sup>-1</sup>), or, flushing time and concentrations within the CRE water column (0.025–0.10 mg L<sup>-1</sup>; Figs. 5c and 6c). There were subtle variations where DIP concentrations were slightly depressed ( $\leq 0.075 \text{ mg L}^{-1}$ ) when inflow was greatest from 2004–05 (Fig. 5c).

The LOICZ budgets indicated that DIN was produced within the CRE ( $\Delta$ DIN > 0.0) in wet season 2003, wet season 2004, and both seasons in 2005 (Fig. 7a). Aside from these instances,  $\Delta$  DIN was near zero for a majority of the 2002–08 budgets averaging 0.006 and 0.052 g N m<sup>-2</sup> d<sup>-1</sup> for the dry and wet seasons, respectively (Table 5). Internal DIN production did not dramatically increase with the loading of external DIN to the CRE despite a maximum rate of 0.25 g N m<sup>-2</sup> d<sup>-1</sup> in the wet season 2003 (Fig. 8a). There appeared to be no net DIN production or consumption (~ 0.0 g N m<sup>-2</sup> d<sup>-1</sup>) by

- <sup>20</sup> There appeared to be no net Div production of consumption (~ 0.0 g Nm<sup>-1</sup> d<sup>-1</sup>) by the CRE when  $T_f \ge 10 d$  (Fig. 9a). Similar to  $\Delta$  DIN, internal  $\Delta$  DIP was positive averaging 0.001 and 0.012 g Pm<sup>-2</sup> d<sup>-1</sup> suggesting that the CRE is either slightly heterotrophic or close to balanced metabolism (-0.05 to -0.47 g Cm<sup>-2</sup> d<sup>-1</sup>) across all seasonal budgets (Table 5 and Fig. 7c). Similar to DIP concentrations, there was no <sup>25</sup> discernable relationship between external DIP loading, or, flushing time and  $\Delta$  DIP
- in the CRE (Figs. 8b and 9b). NEM of the CRE signified a balance between internal production and consumption of primary production over all seasonal budgets. Moreover, average seasonal  $N_{fix}D$  was negative in both the dry  $(-0.003 \, g \, N \, m^{-2} \, d^{-1})$  and wet  $(-0.036 \, g \, N \, m^{-2} \, d^{-1})$  seasons indicating net annual denitrification with an order of



magnitude more occurring in the wet season (Table 5). However, given the overall balanced to slightly heterotrophic metabolism of the CRE, seasonal values for  $N_{fix}D$  did not fluctuate relative to the consistent levels of NEM (Fig. 10a).

# 3.2 St. Lucie Estuary

<sup>5</sup> Rainfall directly to the surface of the SLE ranged from 0.05–0.9 × 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup> across all seasonal budgets (Fig. 3a). Except for the maximum value of 0.9 × 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup> in the wet season 2004, total seasonal rainfall was ≤ 0.1 × 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>. Freshwater discharge to the SLE was highly variable with maximum values of ~ 10 × 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup> in the wet seasons of 2003–2005 followed by minimal inflow for both dry and wet seasons beginning in 2006 (Fig. 3b). Inflow was very low from 2007–08. Basin inflow was proportional surface discharge across all seasons (Fig. 3c).

Salinity in the SLE was inverse to freshwater discharge ranging from 6–20 in both wet and dry seasons from 2002–2004 before values decreasing to values of  $\leq$  2.0 in wet season 2005 (Fig. 4a). The salinity of the SLE decreased from 27.0 to < 2.0 as freshwater inflow increased from 0–10 × 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup> across all seasonal water budgets from 2002–08 (Fig. 5a). Seasonal averages increased to 27.0 in the dry season of 2007 when discharge was lowest and  $T_f = 40$  days (Fig. 6a). Estuary-wide, average DIN concentrations exhibited inter-annual fluctuations similar to patterns of inflow from 2002–08 (Fig. 4b). DIN<sub>e</sub> ranged from 0.09–0.20 mg L<sup>-1</sup> from 2002–05 before increase

- <sup>20</sup> ing to 0.35 mg L<sup>-1</sup> in wet season of 2004. Seasonally averaged DIN concentrations decreased in both dry and wet seasons from 2006–2008. Over all seasonal budgets, the concentration of DIN in the SLE increased linearly from 0.0–0.38 mg L<sup>-1</sup> as external loading approached 0.20 g N m<sup>-2</sup> d<sup>-1</sup> ( $r^2 = 0.85$ ; Fig. 5b). The relationship between flushing time and DIN suggested that concentrations in the SLE declined hyperbolically <sup>25</sup> reaching a minimum of 0.1 mg L<sup>-1</sup> when  $T_f > 10 d$  (Fig. 6b). Wet season DIP concentra-
- tions were generally 2.5 times greater than in the dry seasons from 2002–08 (Fig. 4c and Table 5). DIP<sub>e</sub> concentration reached an apparent saturation at 0.20 mg  $L^{-1}$  with



increased external DIP loading (DIP<sub>Q</sub>) ranging up to 0.4 g N m<sup>-2</sup> d<sup>-1</sup> (Fig. 5c). The hyperbolic relationship for DIP<sub>e</sub> was inverted when  $T_f$  served as the independent variable with concentrations declining as flushing time was > 10 d (Fig. 6c).

- DIN was produced within the SLE ( $\Delta$ DIN > 0.0) in the 2002, 2004 and 2005 wet seasons (Fig. 7a). DIN was consumed the estuary in the wet seasons of 2003 and 2006 and the dry seasons of 2004 and 2005. Internal DIN production increased slightly with external DIN<sub>Q</sub> that included a maximum loading of 0.18 g N m<sup>-2</sup> d<sup>-1</sup> in the wet season 2004 (Fig. 8a). Net estuarine DIN production/consumption hovered near 0.0 g N m<sup>-2</sup> d<sup>-1</sup> when  $T_f \ge 10 d$  (Fig. 9a).
- <sup>10</sup>  $\Delta$  DIP within the SLE was more variable and revealing than patterns of  $\Delta$  DIN. The SLE generally produced DIP in the wet seasons of 2002–04 (Fig. 7b). However, DIP was consumed at rates of -0.05 to -0.30 g P m<sup>-2</sup> d<sup>-1</sup> in 2005 and the dry season of 2006. Internal DIP consumption became more negative (e.g. more consumption) in a linear fashion as DIP<sub>Q</sub> increased to 0.4 g P m<sup>-2</sup> d<sup>-1</sup> (Fig. 8b). Similar to DIN dy-<sup>15</sup> namics,  $\Delta$  DIP was near zero when  $T_f \ge 10d$  (Fig. 9b). Therefore by definition in the LBM, net ecosystem metabolism (NEM) was inverse to internal DIP consumption with maximum values of 1.0–12.0 g C m<sup>-2</sup> d<sup>-1</sup> (Fig. 7c) that increased linearly with the external DIP load (Fig. 8c). Thus, both  $\Delta$  DIP and NEM approached 0.0 when  $T_f \ge 10d$
- (Fig. 9b, c). The average relative difference between N-fixation and denitrifiation (N<sub>fix</sub>D) was positive in both dry (0.109 g N m<sup>-2</sup> d<sup>-1</sup>) and wet seasons (0.347 g N m<sup>-2</sup> d<sup>-1</sup>) in the SLE (Table 5). The proportion of N-fixation (N<sub>fix</sub>D > 0.0) increased linearly with NEM, which increased with external DIP loading (Fig. 10a). Closer inspection revealed that SLE ecosystem metabolism may be sensitive to the DIN : DIP loading ratio as NEM
- $(g C m^{-2} d^{-1})$  and relative N-fixation  $(g N m^{-2} d^{-1})$  decreased to < 0.0 when the molar ratio of externally supplied nutrients is 3 : 1 (Fig. 10b, c). Wet season 2005 had the lowest DIN : DIP loading ratio (~ 1.0), the most NEM (~ 12 g C m<sup>-2</sup> d<sup>-1</sup>), and the greatest relative N-fixation (~ 2.2 g N m<sup>-2</sup> d<sup>-1</sup>).



## 4 Discussion

Coastal water bodies are subjected to anthropogenic delivery of freshwater and inorganic nutrients that are potentially disruptive to internal metabolism (Cloern 2001; Smith, 2006). The Caloosahatchee River and St. Lucie Estuaries on opposite sides

of Florida are small, sub-tropical water bodies with heavily modified watersheds and symptoms of biotic degradation (Barnes, 2005; Sime, 2005). As an initial attempt to quantify the fates of externally loaded N and P, this study generated seasonal DIN and DIP budgets from 2002–2008 for both estuaries. This period of record encompassed a range of seasonal climatic conditions. Nutrient budgets were developed using the LOICZ Biogeochemical Modeling in order to effectively link water, salt, and inorganic nutrient components and understand internal CNP cycling and metabolism at the estuarine ecosystem scale (Gordon et al., 1996; Smith and Hollibaugh, 2006; Liu et al.,

2009). Water column DIN concentrations (DIN<sub>e</sub>) from 2002–2008 were similar between

- the CRE and SLE ranging 0.5–3.5 mg L<sup>-1</sup>. While the CRE responded to external DIN loading by generating internal DIN in seasons of greatest freshwater inflow, this phenomenon was less evident in the SLE as  $\Delta$  DIN increased only slightly with DIN loading. Although DIN<sub>e</sub> was elevated with discharge and loading, concentrations decreased and stabilized in both estuaries as inflow declined and *T*<sub>f</sub> increased to > 10d. The av-
- $_{20}$  erage difference between nitrogen fixation and denitrification (N<sub>fix</sub>D) was negative in the CRE (N<sub>fix</sub> < denitrification) in both seasons with the wet season 10× more negative than the dry season. By contrast, N<sub>fix</sub>D was positive in the SLE (N<sub>fix</sub> > denitrification) in both seasons as wet season rates were 3× greater than in the dry season. Empirically derived measurements from both estuaries in early 2008 support the assertion that
- denitrification is more prevalent and predictable in the CRE relative to the SLE (Howes et al., 2008a, b). This suggests that under the increased temperature, freshwater inflow, and DIN loading indicative of the wet season, the atmosphere is a viable DIN loss pathway for the CRE but not for the SLE. This is likely due to biogeochemical feedbacks



including enhanced coupling of nitrification-denitrification at the sediment-water interface in the CRE (Kemp et al., 2005).

DIP<sub>e</sub> concentrations were greater in the SLE than the CRE as water column DIP in the CRE was more reflective of inter-annual climatic patterns (Childers et al., 2006).

- <sup>5</sup> However, patterns of DIP<sub>e</sub> and Δ DIP in the SLE were correlated to DIP loading but were not so in the CRE. While the SLE phytoplankton demonstrated sensitivity to both DIN and DIP concentrations in controlled bio-assays, it is more probable that hydro-dynamic residence time and not nutrient availability or grazing limited algal biomass accumulation (Phlips et al., 2012). This finding was supported by LOICZ budget results
  <sup>10</sup> as both DIN and DIP concentrations stabilized in both estuaries with flushing times greater than 10 d.
- Compared to the SLE, the CRE appears to be less biogeochemically influenced by inter-seasonal and inter-annual variations in freshwater inflow since it exhibited net heterotrophy or balanced metabolism across all seasonal budgets. While Δ DIP was near 0.0 gP m<sup>-2</sup> d<sup>-1</sup> most of the time in the CRE, the internal DIP concentration, rate of consumption, and net ecosystem metabolism (NEM; g C m<sup>-2</sup> d<sup>-1</sup>) in the SLE increased with external DIP loading. A similar relationship between increased DIP loading and positive NEM has been observed in heavily eutrophied Italian lagoons (Giordani et al.,
- 2008).
  Inorganic nutrient budgets for the SLE suggested intricate relationships between climate, sub-tropical seasonality, water management, inflow and loading, flushing time, and estuarine biogeochemistry (Childers et al., 2006; Howarth and Marino, 2006; Philps et al., 2011). Complex nutrient budget results were expected given the anthropogenic history of the St. Lucie Estuary, the comparatively large ratio between the
  watershed and estuary areas (~ 150), and its present ecological status (see Phase III model in Cloern, 2001; Sime, 2005). While originally a freshwater lake before the late 1800's, the SLE has been impacted by decades of anthropogenic modification of the landscape to the east of Lake Okeechobee for agriculture, flood protection, and urbanization (Fig. 1). Although drainage and discharge typically deliver much of the P



required for primary production in south Florida estuaries (Koch et al., 2012), there is additional potential for internal DIP loading through benthic remineralization (Buzzelli et al., 2013).

- The magnitude of freshwater, DIN, and DIP inputs relative to the flushing time provide the setting for interesting biogeochemical dynamics in the SLE (Dettman, 2001; Sheldon and Alber, 2006). In the absence of freshwater inflow, the flushing time of the SLE is approximately 20 d solely through tidal exchange. If *T*<sub>f</sub> is < 10d as it is much of the time (Ji et al., 2007), then the inputs of freshwater, DIN, and DIP result in rapid DIP consumption, a spike in autotrophy (positive NEM), increased nitrogen fixation, and the potential for DIN export to the coastal ocean. For example, rates of estuarine DIP consumption (-3.0 g P m<sup>-2</sup> d<sup>-1</sup>), NEM (12 g C m<sup>-2</sup> d<sup>-1</sup>), and N<sub>fix</sub>D (2.3 g N m<sup>-2</sup> d<sup>-1</sup>) were all maximized in the wet season of 2005. There is the possibility that fast flushing < 1 d can washout both allochthonous and autochthonous materials from the estuary to the coastal ocean (Doering et al., 2006; Murrell et al., 2007; Phlips et al., 2012). By contrast to washout, longer water residence times allow for grazing and sedimentation that off-</li>
- set autochthonous primary production and stabilize system metabolism (Buzzelli et al., 2007; Lucas et al., 2009; Swaney et al., 2011; Phlips et al., 2012).

Nitrogen loading has contributed to the degraded water quality in the SLE (Sime 2005; SLRPP 2009). N-limitation of phytoplankton in controlled bio-assays on daily time

- scales indicated that reductions in nitrogen loading could decrease primary production in the SLE (Phlips et al., 2012). This result is reasonable given that nitrogen has been emphasized as the dominant limiting nutrient in estuaries (Howarth and Marino, 2006). However, the extrapolation of knowledge gained from fine scale experiments to the seasonal estuary scale may not be appropriate because of feedbacks related to internal historical estuary scale may not be appropriate because of feedbacks related to internal
- <sup>25</sup> biogeochemical cycling (Kemp et al., 2005; Wulff et al., 2011). This may be particularly true for N and P recycling within the SLE.

The nutrient budgets developed in this study demonstrated that biogeochemistry within in the SLE responded to external DIN and DIP loading by increasing net production, nitrogen fixation, and generating excess DIN. It appears that through the sum



of external loading and internal remineralization there is surplus DIN relative to DIP supplies in the SLE. While freshwater inflow stimulates nitrogen fixation requiring P-supply, benthic nitrogen fixation may be inhibited by lack of light penetration (Howarth and Marino, 2006; Buzzelli et al., 2013). The likelihood of substantial nitrogen fixation

- in the SLE may be mitigated because the majority of the phytoplankton community is composed of diatoms with occasional dinoflagellate maxima (Millie et al., 2004; Phlips et al., 2012). Smith (1990) hypothesized that when the potential for nitrogen fixation is low and DIN supply is great, non-heterocystous phytoplankton can proliferate if provided with adequate P-supply. This appears to be the case as the SLE experienced a huge bloom of the toxic, non-heterocystous cyanobacterium *Microcystis aeruginosa*
- with the extreme inputs of freshwater and nutrients in 2005 (Phlips et al., 2012).

The recognition that sub-tropical estuaries have the potential to respond to both N and P inputs is an important step to establish nutrient load limits (Smith et al., 2006; Howarth and Marino, 2006; Wulff et al., 2011). However, merely setting criteria for either

- total or dissolved nutrient loading based on their correlation to water column concentrations fails to appreciate the complexity and uncertainty of estuarine biogeochemical cycling (Dodds, 2003). In both the discharge and the receiving basin, the DIN: DIP ratios are often very different than the TN: TP ratios due to the differential composition and reactivity of dissolved N and P. This is a very important point signifying the necessity to regulate both N and P loading to estuaries (Smith, 2006; Conley et al., 2009;
  - Paerl, 2009). Freshwater inflow to the SLE has a comparatively high TN:

Freshwater inflow to the SLE has a comparatively high TN: TP ratio approaching 14: 1, but a much reduced DIN:DIP ratio of approximately 3.0 (Doering, 1996; SFWMD, 2012a). While most of the TP is available as DIP (DIP:TP = 0.7) and bio-available dissolved organic phosphorus (DOP), most of the TN is in the form of dissolved organic nitrogen (DON) with DIN comprising only 30 % of TN. It is probable that DON is a potentially important component in CNP cycling in sub-tropical estuaries like the SLE and CRE which possesses comparatively low concentrations of water column N (Eyre et al., 2011). Unfortunately, as with most coastal ecosystems, there is a lack of DON



data and understanding at this time (Smith and Hollibaugh, 2006). Establishment of quantitative loading limits for an anthropogenically altered estuary such as the SLE requires an improved understanding of the inter-seasonal and inter-annual relationships among external N and P loading, DON dynamics, planktonic community composition, residence time, benthos and sedimentation, and ecosystem metabolism (Millie et al., 2004; Eyre et al., 2011;Phlips et al., 2012).

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**Table 1.** Primary equations for water, salt, and DIN and DIP budgets using the Land Ocean Interactions in the Coastal Zone (LOICZ) approach.

(1) Estuary water budget	$\frac{\mathrm{d}V_{\mathrm{i}}}{\mathrm{d}t} = V_{\mathrm{Q}} + V_{\mathrm{P}} + V_{\mathrm{G}} + V_{\mathrm{in}} - V_{\mathrm{E}} - V_{\mathrm{out}}$
(2) Net residual flow	$V_{\rm R} = V_{\rm in} - V_{\rm out} = \frac{\mathrm{d}V_1}{\mathrm{d}t} - V_{\rm Q}$
(3) Salt balance	$\frac{\mathrm{d}(V_1S_1)}{\mathrm{d}t} = V_{\mathrm{in}}S_2 - V_{\mathrm{out}}S_1$
(4) Exchange flow	$V_{\rm X} = \frac{1}{(S_1 - S_2)} \left[ V_1 \frac{\mathrm{d}S_1}{\mathrm{d}t} - V_{\rm R} S_{\rm R} \right]$
(5) Flushing time	$T_{\rm f} = \frac{V_{\rm e}}{(V_{\rm X} +  V_{\rm R} )}$
(6) Steady-state assumption	$\frac{dM}{dt} = \sum inputs - \sum outputs + \sum [sources - sin ks]$
(7) Non-conservative substance $(Y)$	$\Delta Y = V \frac{dY}{dt} + > \frac{dV}{dt} - \sum V_{in} Y_{in} + \sum V_{out} Y_{out}$
(8) Photosynthesis-respiration	$106CO_2 + 16H^+ + 16NO_3^- + H_3PO_4 + 122H_2O \rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2$
(9) Net ecosystem metabolism	$[p-r] = -\Delta \text{DIP} \times \left(\frac{C}{P}\right)_{\text{part}}$
(10) Expected net nitrogen change	$\Delta \text{DIN}_{\text{exp}} \equiv (\Delta \text{DIN} + \Delta \text{DON})_{\text{exp}} = (\Delta \text{DIP} + \Delta \text{DOP}) \times \left(\frac{N}{P}\right)_{\text{part}}$
(11) Actual net nitrogen change	$(nfix - denit) = \Delta DIN - \Delta P * (N : P)_{part}$

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**Table 2.** Sources of input data for seasonal DIN and DIP budgets for the Caloosahatchee River Estuary (CRE) and St Lucie Estuary (SLE). Please see text for explanation and details and Fig. 1 for water quantity and quality monitoring locations.

Abbreviation	Definition	Unit	CRE	SLE
$V_{\rm rain}$	Rain to estuary surface	$10^6  \text{m}^3  \text{d}^{-1}$	Nexrad	Nexrad
Vq	Freshwater discharge	10 <sup>6</sup> m <sup>3</sup> d <sup>-1</sup>	DBHydro S-79	DBHydro S484980 + Gordy
V <sub>OFW</sub>	Tributaries + groundwater	10 <sup>6</sup> m <sup>3</sup> d <sup>-1</sup>	Tidal basin model	30 % of total Q
V <sub>e</sub>	Estuary volume	10 <sup>6</sup> m <sup>3</sup>	Interpolated bathymetry	Interpolated bathymetry
S <sub>e</sub>	Estuary salinity	psu	DBHydro CES stations	DBHydro SE stations
S	Downstream bound salinity	psu	Shell Point daily model	DBHydro station SE-11
DIP <sub>rain</sub>	DIP in rain	$mgL^{-1}$	DBHydro averages	DBHydro averages
DIPq	DIP in discharge	$mgL^{-1}$	DBHydro station S-79	DBHydro S-484980
DIP <sub>OFW</sub>	DIP in tributaries + gw	mg L <sup>-1</sup>	Lee County stations	DBHydro S-484980
DIP <sub>e</sub>	DIP in estuary	$mgL^{-1}$	DBHydro CES stations	DBHydro SE stations
DIP。	DIP in downstream bound	$mgL^{-1}$	Lee County Stn. PI-01	DBHydro station SE-11
DIN <sub>rain</sub>	DIN in rain	mg L <sup>-1</sup>	NADP St. Petersburg, FL	NADP St. Petersburg, FL
DIN <sub>Q</sub>	DIN in discharge	mg L <sup>-1</sup>	DBHydro station S-79	DBHydro S-484980
DIN <sub>OFW</sub>	DIN in tributaries + gw	$mgL^{-1}$	Lee County stations	DBHydro S-484980
DIN <sub>e</sub>	DIN in estuary	$mgL^{-1}$	DBHydro CES stations	DBHydro SE stations
DINo	DIN in downstream bound	$mgL^{-1}$	Lee County Stn. PI-01	DBHydro station SE-11



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**Table 3.** Inputs for seasonal dissolved inorganic nitrogen (DIN) and phosphorus (DIP) budgets for the Caloosahatchee River Estuary (CRE). Values are seasonal averages from 2002–2008 used as inputs for water, salt, DIN, and DIP budgets. The wet season consisted of months 6–11 (June–November) within each year. The dry season consisted of month 12 (December) from the preceding year followed by the next 5 months (January–May) the next year. Abbreviations and units shown for average daily input of rain ( $V_{rain}$ ; 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>), upstream flow or discharge ( $V_Q$ ; 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>), and other freshwater sources ( $V_{OFW}$ ; 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>); salinity in the estuary ( $S_e$ ; psu) and downstream or ocean boundary ( $S_o$ ; psu); and concentrations of DIN and DIP in rainfall (DIN<sub>rain</sub> and DIP<sub>rain</sub>), discharge (DIN<sub>Q</sub> and DIP<sub>Q</sub>), the estuary (DIN<sub>e</sub> and DIP<sub>e</sub>), and the ocean boundary (DIN<sub>o</sub> and DIP<sub>o</sub>). All concentrations in mg L<sup>-1</sup> and DIN and DIP in other freshwater sources (DIN<sub>OFW</sub> and DIP<sub>OFW</sub>) were assumed to be equal to those related to freshwater discharge (DIN<sub>Q</sub> and DIP<sub>Q</sub>). See text for specifics and sources of input data for budget development. CRE volume was assumed to be constant ( $V_{CRE} = 140 \times 10^6$  m<sup>3</sup>).

		Water			Salt			DIP			DIN			
Year	Season	$V_{\rm rain}$	Vq	$V_{\rm OFW}$	$S_{\rm e}$	$S_{\rm o}$	DIP <sub>rain</sub>	$DIP_Q$	$DIP_e$	$DIP_{o}$	DIN <sub>rain</sub>	$DIN_Q$	$DIN_{e}$	DIN
2002	Dry	0.1	2.2	0.4	12.6	30.2	0.04	0.16	0.06	0.05	0.75	0.27	0.10	0.04
	Wet	0.5	8.1	0.9	7.9	18.8	0.08	0.09	0.11	0.07	0.96	0.15	0.16	0.15
2003	Dry	0.1	4.6	0.5	8.4	21.7	0.04	0.05	0.05	0.02	0.82	0.15	0.11	0.04
	Wet	0.4	15.4	2.7	8.2	12.5	0.08	0.08	0.06	0.04	0.78	0.14	0.23	0.11
2004	Dry	0.1	4.5	0.4	10.6	24.1	0.04	0.04	0.04	0.02	0.45	0.12	0.12	0.06
	Wet	0.4	13.3	9.3	6.5	17.1	0.08	0.06	0.07	0.03	0.73	0.14	0.18	0.13
2005	Dry	0.2	7.2	0.5	6.2	20.8	0.04	0.03	0.05	0.02	0.74	0.13	0.35	0.12
	Wet	0.5	19.6	2.2	1.6	9.5	0.08	0.05	0.08	0.06	0.58	0.12	0.30	0.19
2006	Dry	0.1	2.2	0.4	1.9	22.6	0.04	0.03	0.05	0.02	1.19	0.15	0.25	0.12
	Wet	0.4	4.2	1.9	7.4	23.1	0.08	0.07	0.11	0.06	0.68	0.14	0.20	0.09
2007	Dry	0.1	0.2	0.3	19.4	33.1	0.04	0.07	0.06	0.02	1.22	0.12	0.16	0.04
	Wet	0.3	0.4	0.8	15.7	31.2	0.08	0.08	0.11	0.01	0.84	0.17	0.10	0.07
2008	Dry	0.1	0.4	0.4	20.0	34.0	0.04	0.07	0.05	0.01	0.77	0.18	0.08	0.03
	Wet	0.5	6.1	2.5	9.1	22.1	0.08	0.08	0.11	0.04	0.77	0.19	0.13	0.05



**Table 4.** Inputs for seasonal dissolved inorganic nitrogen (DIN) and phosphorus (DIP) budgets for the St Lucie Estuary (SLE). Values are seasonal averages from 2002–2008 used as inputs for water, salt, DIN, and DIP budgets. The wet season consisted of months 6–11 (June–November) within each year. The dry season consisted of month 12 (December) from the preceding year followed by the next 5 months (January–May) in the next year. Abbreviations and units shown for average daily input of rain ( $V_{rain}$ ; 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>), upstream flow or discharge ( $V_Q$ ; 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>), and other freshwater sources ( $V_{OFW}$ ; 10<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>); salinity in the estuary ( $S_e$ ; psu) and downstream or ocean boundary ( $S_o$ ; psu); and concentrations of DIN and DIP in rainfall (DIN<sub>rain</sub> and DIP<sub>rain</sub>), discharge (DIN<sub>Q</sub> and DIP<sub>Q</sub>), the estuary (DIN<sub>e</sub> and DIP<sub>e</sub>), and the ocean boundary (DIN<sub>o</sub> and DIP<sub>o</sub>). All concentrations in mgL<sup>-1</sup> and DIN and DIP in other freshwater discharge (DIN<sub>Q</sub> and DIP<sub>Q</sub>). See text for specifics and sources of input data for budget development. SLE volume was assumed to be constant ( $V_{SLF} = 53 \times 10^6$  m<sup>3</sup>).

		Water		Salt			DIP			DIN				
Year	Season	$V_{\rm rain}$	$V_{Q}$	$V_{\rm OFW}$	$S_{\rm e}$	$S_{\rm o}$	DIP <sub>rain</sub>	$DIP_Q$	$DIP_e$	$DIP_{o}$	DIN <sub>rain</sub>	$DIN_Q$	$DIN_{e}$	DIN
2002	Dry	0.03	0.5	0.2	20.3	33.2	0.04	0.10	0.08	0.02	0.75	0.16	0.09	0.06
	Wet	0.06	3.7	1.1	14.2	26.7	0.08	0.12	0.18	0.09	0.96	0.19	0.19	0.15
2003	Dry	0.04	2.9	0.9	17.7	30.6	0.04	0.16	0.08	0.02	0.82	0.19	0.11	0.05
	Wet	0.07	6.2	1.9	5.9	18.0	0.08	0.09	0.18	0.09	0.78	0.23	0.18	0.17
2004	Dry	0.03	2.0	0.6	17.2	30.4	0.04	0.09	0.06	0.02	0.45	0.20	0.07	0.04
	Wet	0.90	7.8	2.4	11.2	25.9	0.08	0.29	0.21	0.1	0.73	0.34	0.36	0.24
2005	Dry	0.05	2.8	0.8	13.8	28.5	0.04	0.38	0.06	0.02	0.74	0.39	0.19	0.04
	Wet	0.10	9.9	3.0	2.3	17.4	0.08	0.70	0.20	0.14	0.58	0.21	0.26	0.21
2006	Dry	0.02	2.2	0.7	14.1	30.8	0.04	0.41	0.07	0.03	1.19	0.33	0.20	0.05
	Wet	0.05	1.0	0.3	19.5	31.9	0.08	0.41	0.18	0.04	0.68	0.70	0.18	0.04
2007	Dry	0.02	0.2	0.1	27.7	35.9	0.04	0.17	0.07	0.01	1.22	0.19	0.02	0.02
	Wet	0.10	1.7	0.5	16.2	33.3	0.08	0.68	0.17	0.02	0.84	0.25	0.16	0.03
2008	Dry	0.04	0.4	0.1	20.2	34.0	0.04	0.23	0.07	0.01	0.77	0.18	0.06	0.02
	Wet	0.10	2.7	0.8	9.4	24.8	0.08	0.87	0.12	0.05	0.77	0.19	0.17	0.11



**Table 5.** Rates of internal dissolved CNP turnover resulting from seasonal DIN and DIP budgets of the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE) from 2002–2008. The CNP budgeting process estimates net internal production or consumption of DIN and DIP through a budgeting process derived from the combined water, salt, and input concentrations ( $\Delta N = g N m^{-2} d^{-1}$  and  $\Delta P = g P m^{-2} d^{-1}$ ). The DIP rate was converted to net ecosystem metabolism (NEM;  $g C m^{-2} d^{-1}$ ) following Eqn. 9 to the relative difference between nitrogen fixation and denitrification ( $N_{fix}$  – Denitrifiation =  $N_{fix}D$ ) with Eqs. (10–11). Average values were calculated across all dry and all wet seasons, respectively.

			CI	RE		SLE					
Year	Season	ΔN	ΔΡ	NEM	N <sub>fix</sub> D	ΔN	ΔΡ	NEM	N <sub>fix</sub> D		
		$gNm^{-2}d^{-1}$	$g P m^{-2} d^{-1}$	g C m <sup>-2</sup> d <sup>-1</sup>	$gNm^{-2}d^{-1}$	$gNm^{-2}d^{-1}$	$g P m^{-2} d^{-1}$	g C m <sup>-2</sup> d <sup>-1</sup>	$gNm^{-2}d^{-1}$		
2002	Dry	0.006	-0.004	0.16	0.03	-0.002	0.003	-0.11	-0.02		
	Wet	-0.001	0.009	-0.37	-0.07	0.011	0.034	-1.39	-0.23		
2003	Dry	-0.001	0.004	-0.16	-0.03	-0.002	-0.0005	0.02	0.002		
	Wet	0.259	0.021	-0.84	0.11	-0.017	0.052	-2.12	-0.39		
2004	Dry	0.003	0.001	-0.06	-0.01	-0.010	0.004	-0.15	-0.04		
	Wet	0.028	0.010	-0.59	-0.08	0.056	0.021	-0.85	-0.09		
2005	Dry	0.044	0.004	-0.17	0.01	-0.010	-0.048	1.97	0.34		
	Wet	0.078	0.010	-0.58	-0.02	0.027	-0.287	11.8	2.10		
2006	Dry	0.004	0.001	-0.05	-0.005	-0.001	-0.068	2.79	0.49		
	Wet	0.010	0.008	-0.33	-0.05	-0.018	-0.002	0.07	-0.01		
2007	Dry	0.001	0.001	-0.03	-0.005	0.001	0.002	-0.07	-0.01		
	Wet	-0.004	0.005	-0.19	-0.04	0.002	-0.034	1.37	0.24		
2008	Dry	-0.001	0.001	-0.04	-0.008	-0.002	-0.001	0.04	0.01		
	Wet	-0.002	0.015	-0.40	-0.11	0.0004	-0.112	3.07	0.81		
Average	Dry	0.006	0.001	-0.050	-0.003	-0.004	-0.016	0.639	0.109		
-	Wet	0.052	0.012	-0.471	-0.036	0.009	-0.047	1.703	0.347		











**Fig. 2.** Box diagrams of salt model (X; upper panel) and non-conservative dissolved substance model (Y; lower panel). Adopted from Gordon et al., 1996. See Table 1 and text for equations and budget description.

Interactive Discussion



**Fig. 3.** Comparative seasonal time series of water budget components for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE). CRE (filled) and SLE (open) bars are paired seasonally with the first pair of each year representing the dry season. All values are in  $10^6 \text{ m}^3 \text{ d}^{-1}$ . (A) Rainfall; (B) discharge; (C) tributaries + ground water.





**Fig. 4.** Comparative seasonal time series of water budget components for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE). CRE (filled) and SLE (open) bars are paired seasonally with the first pair of each year representing the dry season. **(A)** Salinity (psu); **(B)** DIN (mg L<sup>-1</sup>); **(C)** DIP (mg L<sup>-1</sup>).





**Fig. 5.** Scatter plots from seasonal DIN and DIP budgets for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE) from 2002–2008. **(A)** Freshwater discharge ( $V_Q$ ) vs. estuary salinity (psu); **(B)** external DIN load ( $g N m^{-2} d^{-1}$ ) vs. estuary DIN concentration ( $mg L^{-1}$ ); **(C)** external DIP load ( $g P m^{-2} d^{-1}$ ) vs. estuary DIP concentration ( $mg L^{-1}$ ). Regression lines,  $r^2$  values, and equations provided for the SLE points only.





**Discussion** Paper **Discussion Paper** Fig. 6. Scatter plots from seasonal DIN and DIP budgets for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE) from 2002–2008. Estimated flushing time (T<sub>f</sub>; days) provided the independent variable vs. (A) salinity (psu); (B) estuary DIN concentration (mg  $L^{-1}$ ); (C) estuary DIP concentration (mg L<sup>-1</sup>). Regression lines,  $r^2$  values, and equations provided for the SLE points only. 2409





**Fig. 7.** Comparative seasonal time series of internal CNP source/sink processing for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE). CRE (filled) and SLE (open) bars are paired seasonally with the first pair of each year representing the dry season. **(A)**  $\Delta$  DIN (gNm<sup>-2</sup>d<sup>-1</sup>); **(B)**  $\Delta$  DIP (gPm<sup>-2</sup>d<sup>-1</sup>); NEM (gCm<sup>-2</sup>d<sup>-1</sup>). See Table 1 for CNP equations.





**Fig. 8.** Scatter plots from seasonal DIN and DIP budgets for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE) from 2002–2008. **(A)**  $\Delta$  DIN (gNm<sup>-2</sup>d<sup>-1</sup>); **(B)**  $\Delta$  DIP (gPm<sup>-2</sup>d<sup>-1</sup>); NEM (gCm<sup>-2</sup>d<sup>-1</sup>). External DIN load (gNm<sup>-2</sup>d<sup>-1</sup>) or DIP load (gPm<sup>-2</sup>d<sup>-1</sup>) provided the independent variable. Regression lines,  $r^2$  values, and equations provided for the SLE points only.





**Fig. 9.** Scatter plots from seasonal DIN and DIP budgets for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE) from 2002–2008. Estimated flushing time ( $T_f$ ; days) provided the independent variable vs. **(A)**  $\Delta$ DIN (gNm<sup>-2</sup>d<sup>-1</sup>); **(B)**  $\Delta$ DIP (gPm<sup>-2</sup>d<sup>-1</sup>); NEM (gCm<sup>-2</sup>d<sup>-1</sup>).





**Fig. 10.** Scatter plots from seasonal DIN and DIP budgets for the Caloosahatchee River Estuary (CRE) and St. Lucie Estuary (SLE) from 2002–2008. **(A)** Both the CRE (filled circles) and the SLE (open squares) presented with net ecosystem metabolism (NEM) vs. the difference between nitrogen fixation and denitrification ( $N_{fix}$ D). Regression lines,  $r^2$  values, and equations provided for the SLE points only. **(B)** Scatter plots of seasonal values from the SLE from 2002–2008. Relationship between the DIN:DIP ratio of loading (independent) and the difference between nitrogen fixation and denitrification ( $N_{fix}$ D; dependent). **(C)** Relationship between the DIN:DIP ratio of loading as the independent variable and net ecosystem metabolism (NEM) as the dependent variable.

